



High-performance of PbO₂ nanowire electrodes for lead-acid battery



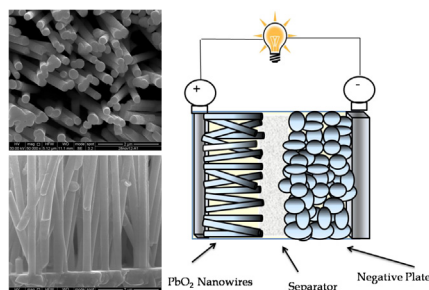
A. Moncada, M.C. Mistretta, S. Randazzo, S. Piazza, C. Sunseri, R. Inguanta*

Laboratorio di Chimica Fisica Applicata, Dipartimento di Ingegneria Chimica Gestionale Informatica Meccanica, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

HIGHLIGHTS

- PbO₂ nanowires exhibited excellent performance in lead-acid battery.
- Nanowires were obtained by a simple template electrodeposition.
- An almost constant capacity of about 190 mAh g⁻¹ was delivered at 1C.
- PbO₂ nanowires showed a very good cycling stability for more than 1000 cycles.
- Nanowires morphology changed significantly over cycling.

GRAPHICAL ABSTRACT



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ABSTRACT

PbO₂ nanowires were obtained by template electrodeposition in polycarbonate membranes and tested as positive electrode for lead-acid battery. Nanowires were grown on the same material acting as current collector that was electrodeposited too. The nanostructured electrodes were assembled in a zero-gap configuration using commercial negative plate and separator. Cell performance was tested by galvanostatic charge/discharge cycles in a 5 M H₂SO₄ aqueous electrolyte. PbO₂ nanostructured electrodes were able to deliver at 1C rate an almost constant capacity of about 190 mAh g⁻¹ (85% of active material utilization), close to the theoretical value (224 mAh g⁻¹). The nanowire array provides a very large surface area (about 70 times higher than the geometrical one) that enhances the specific capacity of the battery. SEM images of the as-prepared and cycled electrodes showed that nanowires morphology changes significantly after the initial cycles. Change of morphology led to the formation of very spongy structure, characterized by the presence of macro-voids, which ensured penetration of the electrolyte in the inner areas of the electrode. Besides, PbO₂ nanowires showed a very good cycling stability, maintained for more than 1000 cycles. These findings indicate that this new type of electrode might be a promising substitute of positive plates in lead-acid battery.

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1. Introduction

Lead-acid batteries can accumulate energy for long periods of time and deliver high power. The raw material for their production is unlimited and about 95% of the material battery can be recycled [1]. However, the currently marketed lead-acid batteries can

deliver a specific energy of only 30–40 Wh kg⁻¹ at a maximum rate of C/5 [2]. These features limit their use in the most advanced applications, where high specific energy and cycling rate are requested.

The low specific energy is due to the combined effects of high atomic weight of the lead and low utilization degree of the usual pasted electrodes. In turn, a low cycling rate is mandatory owing to the particular morphology of commercial battery electrodes, consisting of lead grids supporting the two pasted active materials, that during charge/discharge are subjected to the desulphation–

* Corresponding author. Tel.: +39 09123863732; fax: +39 09123860841.
E-mail address: rosalinda.inguanta@unipa.it (R. Inguanta).

sulphation reactions. During discharge, paste thickening progressively hinders electrolyte transport toward the inner electrode regions making the sulphation reaction through the electrode thickness progressively incomplete. Paste thickening is due to the formation on both electrodes of lead sulphate, which occupies a larger volume than both lead and lead dioxide [3]. In addition, the repetitive volume changes cause mechanical instability of the plates determining the crumbling of the active pastes, with further progressive loss of capacity. For these reasons, lead-acid batteries are not suitable for the most innovative applications, such as electric mobility, where they can be used only in micro-hybrid cars, i.e. cars equipped with a start-stop system [4–7].

The drawback of lead-acid battery could be overcome, likely, by employing electrodes with nanostructured active materials. In fact, nanostructured electrodes are alternative to the conventional ones for their high aspect ratio and surface area allowing fabrication of lightweight batteries with high specific energy [8–12]. Besides, nanostructured electrodes are essential to fabricate micro- and nano-batteries [13,14], suitable for biomedical applications [15]. Many examples can be found in the literature on fabrication and testing of nanostructured electrodes obtained with different methods [[8–12,16–19] and references therein]. In particular, template electro-synthesis appears a very useful technique because easy to conduct and cheap [11,20]. We have employed this fabrication method to obtain nanostructured SnCo electrodes [21,22] showing very good performance as anode in lithium-ion batteries [23,24]. Starting from these satisfying findings, we have extended the use of nanostructured electrodes to lead-acid batteries.

Initially, anodic alumina membrane was thought as template, because of its regular morphology and high pore density, therefore we studied template electrodeposition of PbO₂ [25,26] and Pb [27] nanowires in this type of membrane. But, as shown in Ref. [23], electrochemical reactions during charge/discharge cycles produce a continuous variation of nanowires volume making the nanostructured electrodes mechanically fragile. To overcome this problem, in our previous study, we changed anodic alumina membranes with polycarbonate ones [24], in order to increase the free-space between nanowires for better accommodating volume expansion/contraction during cycling. Besides, the larger free-space ensures a better electrolyte permeation through the nanostructured electrode leading to a higher utilization degree of the active materials. Finally, a quick template dissolution can be conducted in suitable organic solvent for making clear the nanostructure. The dissolution process is so simple that it can be scaled easily for industrial purpose. In addition, both solvent and polycarbonate, can be easily recovered by simple distillation at low temperatures, and completely recycled, unlike alumina.

We have grown PbO₂ and Pb nanowires by electrodeposition in polycarbonate templates following a two-step procedure leading to arrays of nanowires well attached to a current collector made of the same material [28]. The present work is a part of a systematic investigation on the growth and electrochemical performance of these nanowires as electrodes for lead-acid battery. Here, the results concerning PbO₂ nanowires will be presented and discussed. At our better knowledge, is the first time, after the preliminary investigation reported in our recent paper [29], that results relating to the fabrication and possible application of these type of electrodes are shown. Up to date, only nanostructured electrodes consisting of PbO₂ thin film [30], or nanoparticles [31] or microspheres [32] were proposed.

2. Experimental

Commercially track-etched polycarbonate membranes (Whatman, Cyclopore 47) were used as template. Nominal pore diameter,

thickness and pore density were 200 nm, 20 μm and about 10^{12} pores m^{-2} , respectively, but according to our SEM investigation, the true average thickness was about $16 \pm 0.65 \mu\text{m}$, whilst the mean diameter ranged from 180 to 250 nm. Pore population density was $3 \div 6 \cdot 10^{12}$ pores m^{-2} .

Prior to deposition, a very thin layer of Au was sputtered onto one surface of the membrane to make it conductive. Nanostructured electrodes were obtained by a two-step procedure using a modified Sovirel[®] cell [33]. In the first step, a uniform and thick layer of PbO₂ was electrodeposited onto the Au-coated side of the membrane at room temperature under a constant current of 10 mA cm^{-2} up to a charge of 80 C cm^{-2} . During the second step, PbO₂ nanowires were grown inside membrane channels at 60°C applying a constant potential of 1.5 V (SCE) up to 8 C cm^{-2} . Both electrodepositions were performed from an aqueous solution of 1 M Pb(NO₃)₂ and 0.3 M H(NO)₃ using a PAR Potentiostat/Galvanostat (mod. PARSTAT 2273) connected to a PC and controlled by POWERSUITE[™] software.

After electrodeposition, polycarbonate membrane was dissolved in CHCl₃ to obtain a nanostructured electrode consisting of PbO₂ nanowire array electrically connected to the current collector. The active mass of nanowires was evaluated by gravimetric measurements using a Sartorius microbalance (mod. Premium Microbalance ME36S).

Nanowires characterization was conducted by XRD, EDS, RAMAN and SEM, as detailed elsewhere [25–28]. In addition, electrode wettability was evaluated by contact angle measurements in a 5 M aqueous solution of sulphuric acid as wetting liquid, using a FTA 1000 (First Ten Ångströms) instrument. Contact angle was measured on different areas of the nanostructured electrodes to evaluate their uniformity. All electrode characterizations were performed before and after the electrochemical tests, in order to evaluate possible occurrence of electrode changes.

Electrochemical performances were tested in a 5 M sulphuric acid aqueous solution, after assembling nanostructured lead oxide in a zero-gap configuration using a commercially available negative plate and separator (AGM type). Typically, the negative electrode consisted of metallic lead in a high porous structure. The negative active mass was supported by highly pure Pb–Ca (0.1% w/w)–Sn (0.45% w/w) casted grid. Negative plates were replaced every 200 cycles. Charge/discharge cycles were carried out by means of a multi-channel cell test system (Solartron, 1470E) at room temperature. Data were acquired and processed by using MULTISTAT[™] and CorrView2[™] software, respectively. Charge/discharge cycles were performed at 1C rate with a cut-off potential of 1.2 V and the cell was discharged up to 90% of the gravimetric charge of PbO₂ electrode. Only nanowire weight was considered, because it was preliminary checked that current collector was not involved in the conversion reactions occurring under cycling. The geometrical area of the nanostructured electrodes was 2.2 cm^2 . In all batteries, negative plates had more electro-active material and more effective surface area than the positive electrode, in order to ensure that this one was really determining the performances of the battery.

3. Results and discussion

3.1. Growth and characterization

As reported in the experimental section, nanostructured electrodes were fabricated by a two-step procedure. The first step consisted in galvanostatic deposition of a very uniform and compact layer of PbO₂ with a thickness of about $77 \pm 1.4 \mu\text{m}$ onto the membrane side previously sputtered with gold. We found that the current collector weight was very close to the value of 1.24 mg C^{-1} ($1.23 \pm 0.03 \text{ mg C}^{-1}$) corresponding to deposition

current efficiency of 100% [34]. This layer has a fundamental role because it acts as both current collector and mechanical support for nanowires that were electrochemically deposited during the subsequent step.

Fig. 1 shows the growth curves of PbO_2 nanowires in polycarbonate template: all depositions were carried out up to a charge of 8 C cm^{-2} . Three of the four different current regimes, typical of potentiostatic growth of nanowires in nanoporous membrane [[35] and references therein], can be observed. The initial very rapid current decrease (first regime) was due to the charging of the electric double layer and subsequent development of a diffusion layer at the electrode/solution interface. Region where current density is almost constant (second regime) corresponds to the growth of nanowires within the pores of the membrane. The third regime, consisting in an increase of current for long deposition times, was shown only by 1 and 4 samples. The current increase following the constant current region has been attributed to the formation of caps outside membrane pores, whose presence was confirmed by SEM analysis. The minor differences between the curves are due to statistical variations in the morphological parameters of each membrane (thickness, mean diameter, pore population density), as well as to the non-perfectly identical electrochemical conditions at pore base [36]. Only samples without superficial caps, like 2 and 3, were tested as electrodes in battery.

About the crystallographic nature of the deposit, it was found that current collector was a mixture of α and β PbO_2 phases, whilst nanowires consisted of pure β phase (Fig. 2), in agreement with the literature data [[25,34] and references therein]. These results were confirmed also by Raman spectroscopy.

SEM images of Fig. 3 show the cross sections of the nanostructured electrodes at different magnifications (a–c) and the top view of the nanowires (d). Fig. 3a clearly shows the current collector uniformly covered by PbO_2 nanowires. The collector appears continuous, uniform, compact and free of cracks or fractures. The high magnification image of Fig. 3b shows that nanowires are firmly connected to the current collector. Fig. 3c highlights the nanowires morphology, featured by a cylindrical shape fairly regular and slightly wrinkled. Image analysis of this picture gave a real surface about 70 times larger than the geometrical one. Interconnection between different wires, which is a characteristic of polycarbonate template channels, is also clearly visible. In both Fig. 3b and c, some wires are broken due to sample preparation for SEM analysis. Fig. 3d shows the top view of the nanostructured

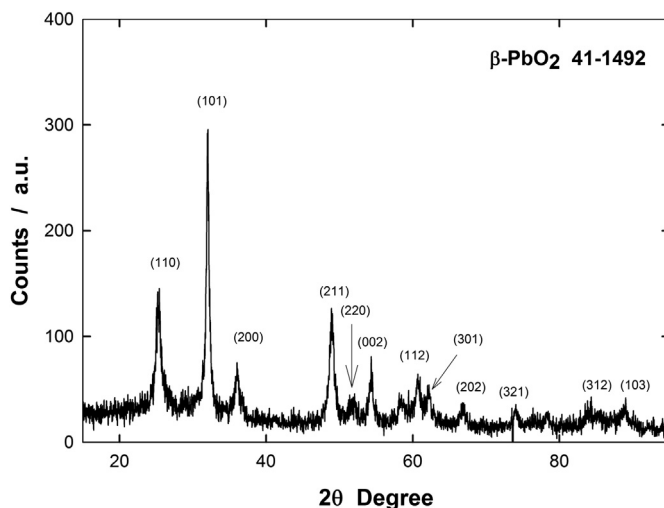


Fig. 2. XRD patterns of a PbO_2 nanostructured electrode after total dissolution of template.

electrodes, where wire of different diameters are clearly visible. From this image, we calculated an average diameter of 250 nm, quite different from the nominal diameter of the template. Mean length of the wires was about 15 μm .

3.2. Electrochemical tests

As known in the literature [1,37], the first battery charge requires high attention to ensure proper working and long life. Charging rate must be low enough in order to prevent high values of cell voltage driving gas production. In the literature, various battery start-up procedures are proposed, employing constant voltage or current, or a combination of both, whose duration is several hours (in some cases even days), for limiting voltage increase and consequent gas evolution [1]. This last reaction must be avoided for several reasons: 1) it exerts a mechanical action on the plate surface, that in long runs causes fall of active material, with consequent sludge production and decrease of capacity; 2) it wastes electric energy and water, which must be replenished; 3) acid solution droplets, transported by evolving gas, cause a considerable reduction of battery electrical insulation and corrosion of metallic contacts.

To avoid these problems, we have employed for the first charge a multi current step procedure, with a step-wise increase of the current from a value equal to $\text{C}/5$ up to 1C . Each step lasted for a time enough to deliver an electric charge equal to the gravimetric capacity of the nanostructured electrode. As shown in Fig. 4, which reports the first charge/discharge cycle, the gradual current rise corresponds to a gradual increase of cell voltage without any spikes. This issue is of fundamental importance for the mechanical stability of our nanostructured electrodes because, in addition to the above mentioned drawbacks, gas evolution is very dangerous for nanostructured electrodes, because it can cause detachment of some bundles of nanowires and, in many cases, also current collector fracture.

After the first cycle, nanostructured PbO_2 electrode was tested at 1C , room temperature and a discharge of 90% of the gravimetric capacity. The cut-off voltage, that is fundamental for the reliability of the results, was chosen in dependence on the C-rate. In particular, for cycling at 1C , a cut-off potential in the range from 1.6 to 0.7 V is suggested [1]. Accordingly, we choose 1.2 V corresponding to a deep discharge, in order to check the lifetime in more severe

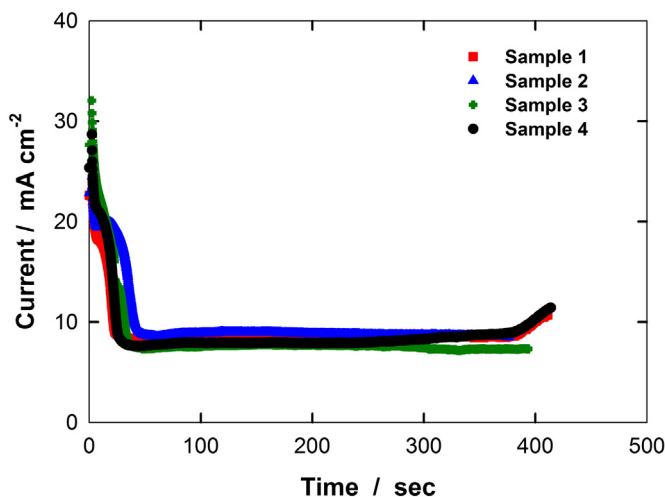


Fig. 1. Growth curves of PbO_2 nanowires inside the channels of a polycarbonate membrane obtained at 60°C and 1.5 V (SCE) up to 8 C cm^{-2} .

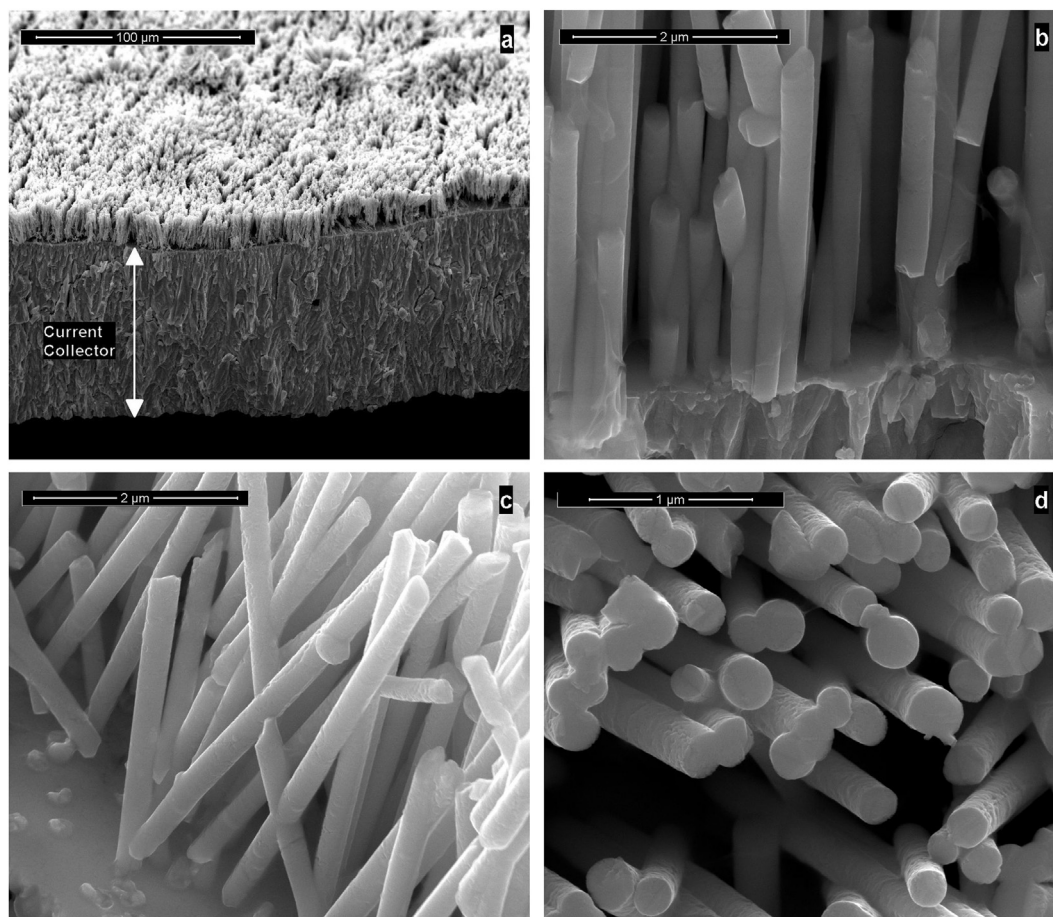


Fig. 3. SEM images of a PbO_2 nanostructured electrode after total dissolution of template: (a–c) cross-sectional views; (d) top-view.

discharge conditions. In this context, it is useful to highlight a significant difference with commercial batteries. Since they usually work at C/10, a cut-off potential between 1.7 and 1.3 V is suggested [1]. In practice, a cut-off voltage between 1.75 and 1.8 V, i.e. above the higher limit, is selected in order to avoid a deep sulphation of the active pastes, which would lead to a rapid death of the battery. To prefer conservative conditions in terms of discharge depth enhances battery lifetime, but reduces the utilization degree of the active materials, with consequent low values of specific energy. On

the contrary, we were interested in checking the lifetime in the presence of fast cycling with deep discharge. i.e. in more severe conditions than commercial batteries.

Fig. 5 shows efficiency and discharge capacity as functions of cycle number. Initially, performance of the nanostructured PbO_2 electrodes improved under cycling. This behaviour is common to lead-acid battery and was associated to a change in the active

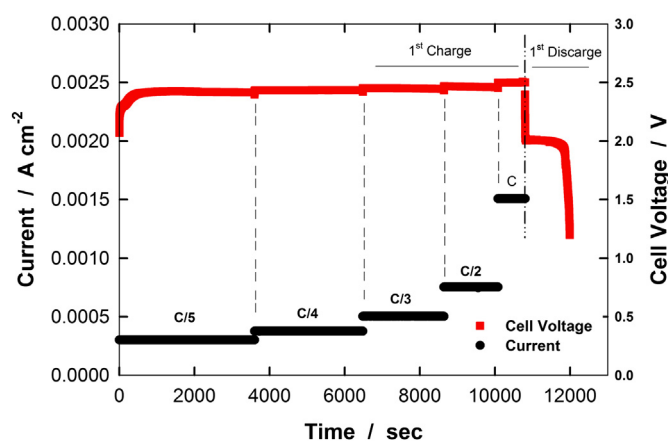


Fig. 4. First charge–discharge cycle with a step-wise increase of the charge current.

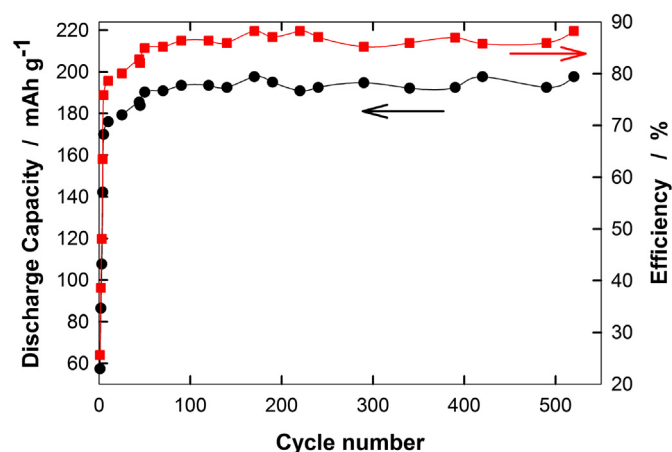


Fig. 5. Discharge capacity and efficiency at 1C for a PbO_2 nanostructured electrode vs. numbers of cycles.

material morphology, as reported in the literature [30] and references therein], and here detailed below. This stabilization phase is accomplished in approximately 50 cycles at 1C, a small fraction of the electrode lifetime. After this period, a discharge capacity of about 190 mAh g^{-1} was delivered and a good stability was maintained for over 1000 cycles. A very important issue to emphasize is that our electrodes got efficiency values between 85 and 90%, that are higher than that of pasted PbO_2 electrodes whose maximum discharge efficiency does not exceed 50%, in the best case. Up to now, only Morales et al. have reported similar good results with PbO_2 nanoparticles [31]. Their electrodes are capable to deliver a capacity of 160 mAh g^{-1} at 1C for 280 cycles.

Fig. 6 shows charge/discharge curves at different cycles: charge curves of Fig. 6a show that, after an initial transient, in the first cycles potential rises up slightly with the charging time. Besides, charge voltage decreases gradually with increasing cycles and it stabilizes at a practically constant value already after 30 cycles. No spike or rapid rise of voltage, due to gas evolution, is present.

Fig. 6b shows that most of the electric charge is delivered at a quasi-constant voltage, with a drop of only 100 mV. Since negative electrode mass is largely in excess, the voltage plateau during discharge can be related to the conversion reaction of PbO_2 electrode to PbSO_4 [37,38]. This finding is very important in the field of the energy storage, because it implies a quasi-constant energy

supply during fast discharge too. Due to the high surface/volume ratio typical of the nanostructured morphology, the conversion reaction involves almost entirely the electrode active mass, determining high discharge efficiency also at high C-rate, unlike conventional lead-acid battery. In the final stage of discharge, voltage rapidly drops to the cut-off potential. In conventional lead-acid battery, this behaviour has been attributed to the progressive depletion of H_2SO_4 due to the conversion reaction. In particular, H_2SO_4 reaching the inner part of the pasted electrode is exhausted and non-compensated by flow of fresh acid from the bulk of the electrolyte. In the depleted zones, electrolyte pH increases and PbO_2 reduces to PbO_n ($1 < n < 1.5$). Since PbO_n has high electrical resistance, its formation causes a rapid decrease of discharge voltage toward the cut-off potential [37,38]. In the case of nanostructured electrode, Fig. 6b shows that the final voltage drop is rather progressive at low cycle number, whilst becomes very sharp after the 50th cycle. This behaviour, together with the increase of drained charge under cycling, can be explained by considering also the wettability of the active material. In particular, contact angle on the top surface of the nanostructured electrode was measured before and after cycling, using 5 M sulphuric acid as wetting liquid. Fig. 7 shows that contact angle changes from 105° , for the as prepared electrode, to 18° , for the electrode after 100 charge/discharge cycles; indicating that electrode wettability increases under cycling likely due to hydration of the surface coupled with the morphological change (inset of Fig. 7).

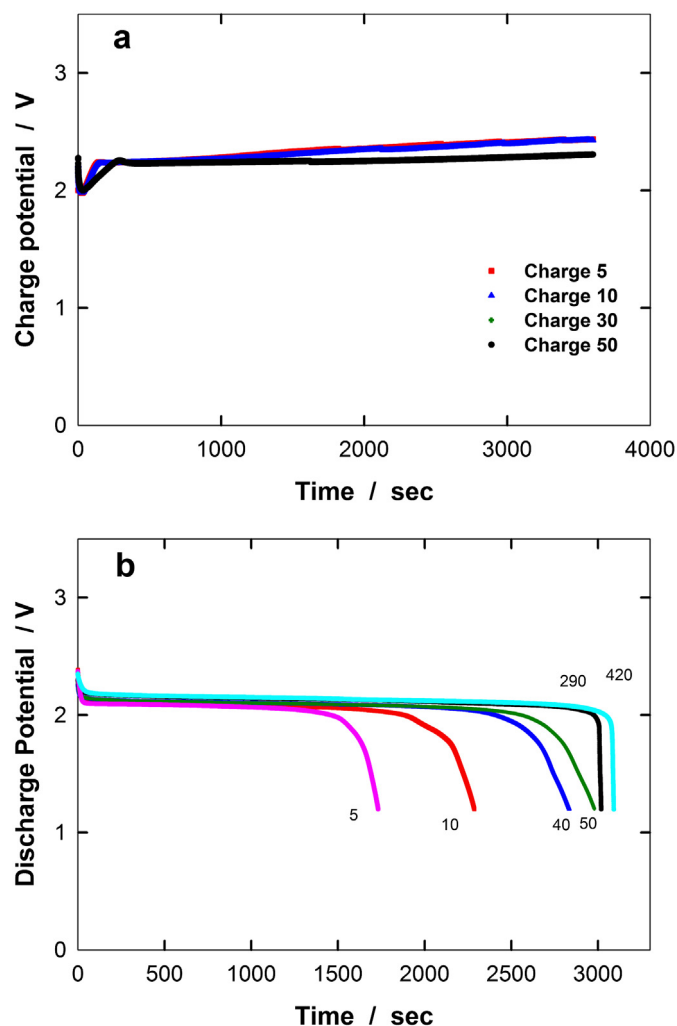


Fig. 6. (a) Charge and (b) discharge curves at 1C for different cycles for a PbO_2 nanostructured electrode.

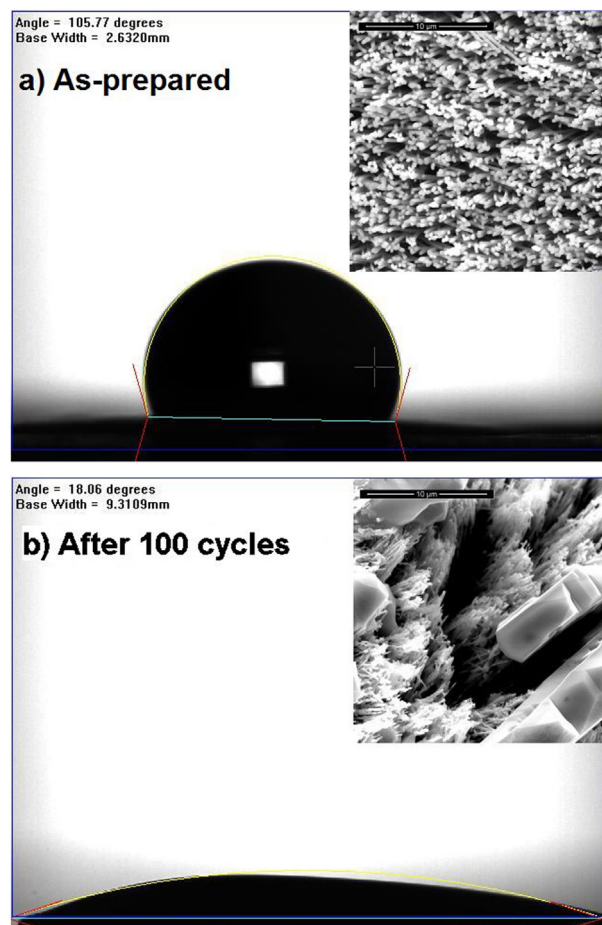


Fig. 7. Contact angle measured on: (a) as prepared electrode (b) electrode after 100 charge/discharge cycles. In the insets SEM images of the electrode top surface are shown.

On this basis, it can be assumed that H_2SO_4 solution initially wets nanowires only in their outer part. Since the area exposed is small, rapidly it is converted to PbSO_4 that being electrically insulating leads to the voltage drop toward the cut-off value. This justifies the low charge drained during initial cycles. In addition, the area wetted by the solution is not perfectly delimited, but, likely, there is a progressive transition from wet to non-wetted areas, therefore, also PbO_2 was progressively converted to PbSO_4 determining the smooth voltage decay up to about the 50th cycle, as shown in Fig. 6b. As nanowires wettability increases, also the charge drained on discharge increases up to the steady state of Fig. 6b. In these conditions, likely, H_2SO_4 solution fully permeates PbO_2 nanowires, consequently, final potential drop occurs sharply as soon as active mass is entirely converted to PbSO_4 . Therefore, we can say that nanostructured morphology allows both high cycling rate and high charge/discharge efficiency. In the subsequent charge of the nanostructured electrode, potential peak appearing at the beginning of the charge (Fig. 6a) is proper due to this high resistive layer, whose re-oxidation causes the charge potential decrease visible in the initial part of the charge curves of Fig. 6a.

The discharge curves of Fig. 6b clearly show that the drained battery capacity was increasing with the number of cycles. From 50th to 290th cycle, battery capacity increases and discharge curves progressively assume the shape of 290th; while between the 290th and 420th cycle discharge curves do not show appreciable differences. Similar trend was observed also in commercial batteries but at lower C rate [1,39] It is important to highlight that these very

good performances were obtained directly from as prepared nanostructured electrodes, without the curing and formation process necessary for conventional pasted electrodes.

As mentioned above, the increase of the battery capacity is attributable to a change of electrode morphology under cycling, clearly visible in the SEM images of Fig. 8 (after 1 cycle) and 9 (after 100 cycles). This change is due to the nanowires volume variations owing to conversion of lead sulphate to lead oxide and vice-versa.

In the cross section views of Figs. 8a–b and 9a, the current collector appears undamaged, without cracks or any modification in the morphological features. This is an important finding, because it confirms that collector did not undergo any volume expansion and therefore did not participate to the electrochemical reactions. Besides, Figs. 8b and 9b show that even if the morphology of nanostructures was changed, the nanowires were still attached to the current collector. After one charge/discharge cycle (Fig. 8c–d) nanowires present a very rough morphology. This morphological variation entails additional advantages for the active material, which maintains a high surface area for the occurrence of the electrochemical reactions. As seen from the SEM image of Fig. 8c, the nanostructured electrode is characterized by a high degree of porosity that strongly facilitates transport of ions and water towards the surface of the active material. If we compare active material morphology of the conventional plate [2] with that of our electrode after cycling, we observe that nanostructured electrode presents a higher porosity, favoured by geometry of nanowires array. Real surface area is much higher in our case, this implies that

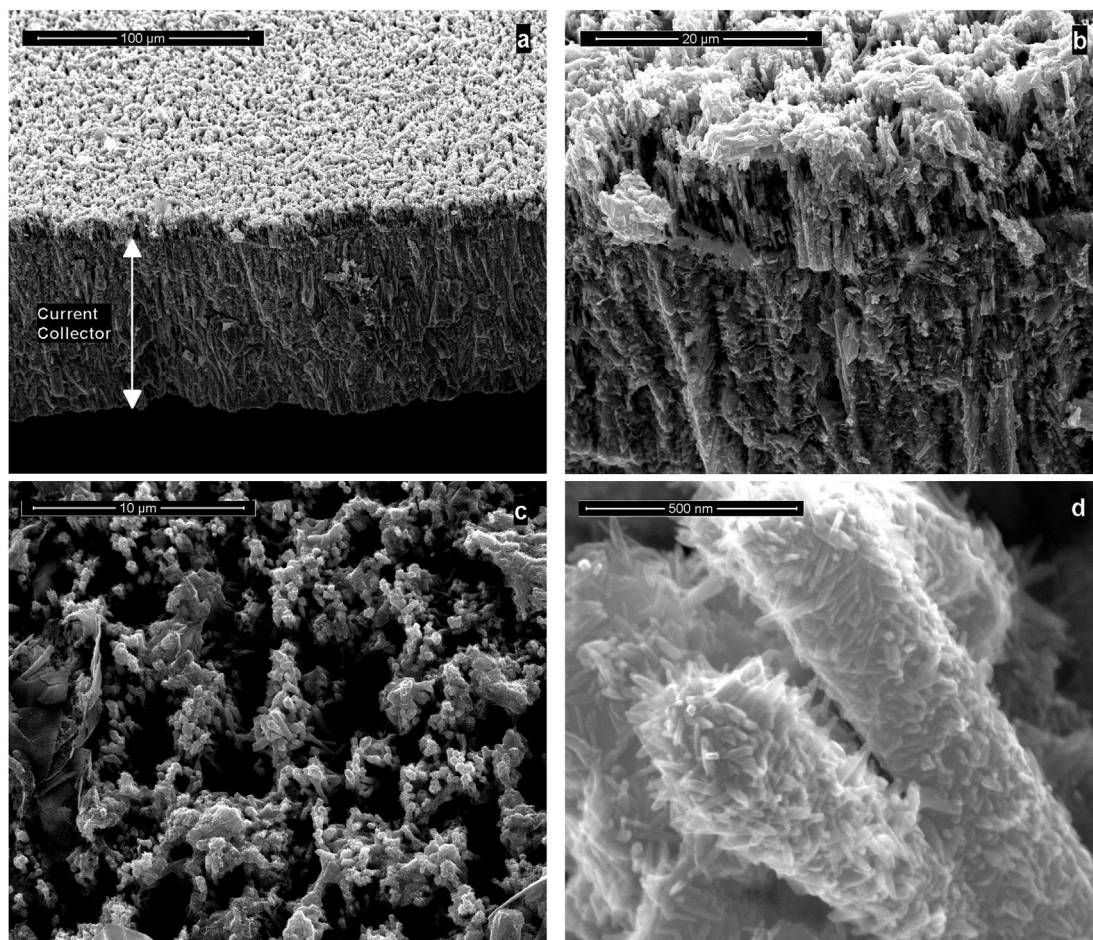


Fig. 8. SEM images of a PbO_2 nanostructured electrode after 1 charge/discharge cycle at 1C: (a–b) cross-sectional views; (c) top-view; (d) high magnification of PbO_2 nanowires.

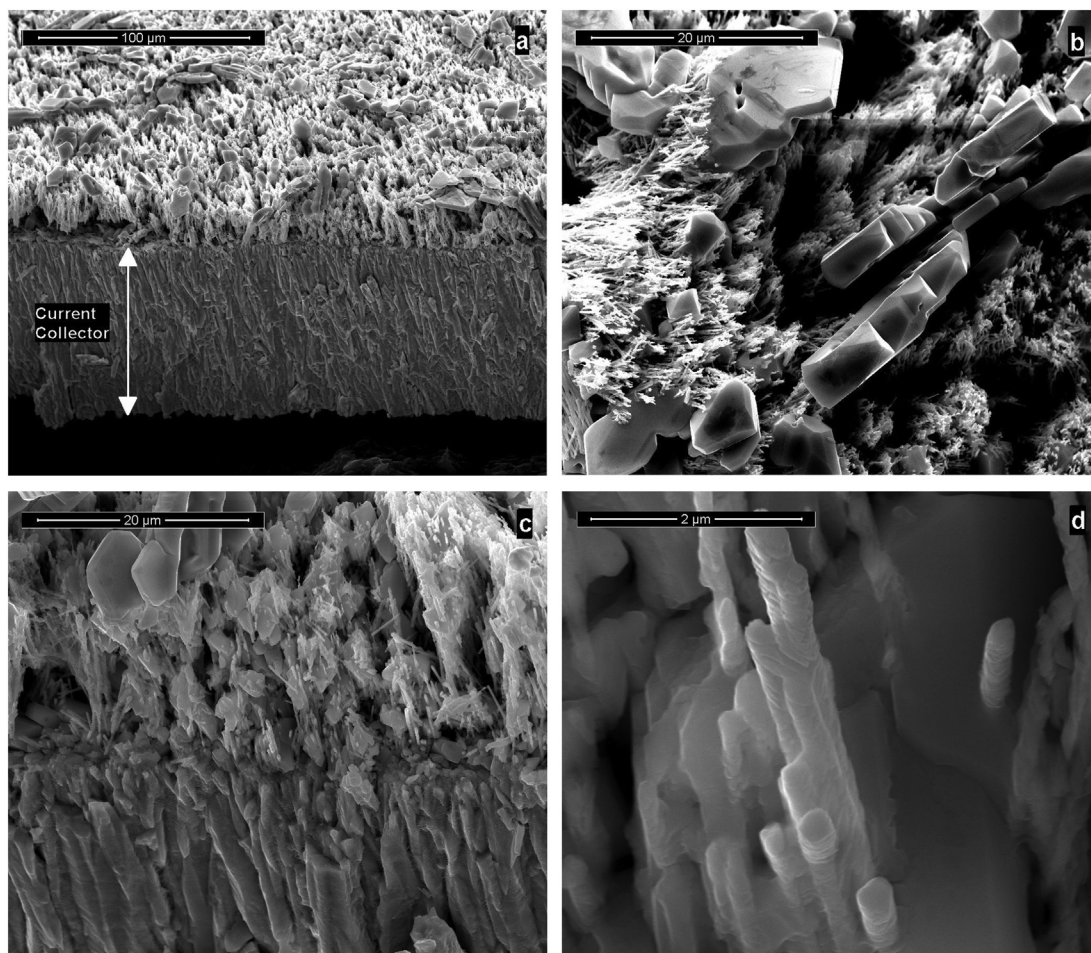


Fig. 9. SEM images of a PbO_2 nanostructured electrode after 100 charge/discharge cycles at 1C: (a–b) cross-sectional views; (c–d) top-view of PbO_2 nanowires.

much more charge can be delivered, and then a higher degree of utilization of the active material (about 85% vs. 30% of the commercial battery) is accomplished. In fact, the whole lateral area of the nanowires is accessible to the electrolyte and thus available for the electrochemical reactions. Similar conclusions were also reached by several authors for nanostructured PbO_2 thin films [30,32,40–42]. In the case of conventional plates, because the “dough” of powders has tendency to compact, the variation of the morphology leads to a stable skeleton structure having scarce porosity; as a consequence, the inner core is never in contact with the electrolyte.

Electrode morphology was changing under cycling and after 100 cycles, the morphology of Fig. 9 was found. Clearly, these images show that the active material still presents a good porosity, a sort of meso-porous structure is formed, and is almost entirely available for electrochemical reactions. Fig. 9a and b shows the presence of macro-crystals of lead sulphate on the electrode surface, but, practically, Fig. 9c and d shows a morphology almost similar to the initial one, where bundles of nanowires are still visible although they have a much more pronounced roughness. This behaviour can be associated to wettability variation of the electrodes under cycling, above discussed (Fig. 7).

4. Conclusions

In this work, PbO_2 nanowires for application as positive electrodes in lead-acid batteries were fabricated. The basic idea was to

exploit the role of the enormous surface area characterizing the nanostructures in order to increase specific energy and active material utilization at high C-rate, in order to extend the use of these electrodes to electric traction. With the aim to achieve these objectives, we fabricated nanostructured electrodes through electrodeposition in nanoporous template. The electrodes were assembled in a zero-gap configuration, and tested in a 5 M sulphuric acid solution at a 1C rate, room temperature and a deep discharge of 90% of the PbO_2 gravimetric capacity.

We found that nanostructured PbO_2 electrodes were able to deliver a discharge capacity of 190 mAh g^{-1} at 1C that was maintained for over 1000 cycles. Discharge curves show that most of the process occurred at a constant voltage. These findings are very encouraging because they were never found before in commercial batteries, even at lower C-rate. Besides, these performances were obtained without performing any curing and formation process that are, instead, necessary for conventional plates.

Similarly to what happens in the conventional plates, nanostructures undergo a significant morphology change, due to the conversion reactions (sulphation/desulphation) occurring during the charge/discharge cycles. Morphology change led to the formation of very spongy and non-compact meso-porous structures, characterized by a considerable presence of macro-voids, which ensure the penetration of the electrolyte also in the inner electrode areas.

This conclusion is also confirmed by contact angle measurements showing an increase of electrode wettability under cycling,

due to a likely progressive hydration of the electrode, determining an increase of its hydrophilic character. Thus, during the charge/discharge cycles most of the active mass of the electrode becomes easily accessible to the electrolyte, and this implies a high degree of utilization of the material (about 85%) leading to the excellent performances shown in this work.

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